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Molecular Characterization of Polymethyl Acrylate in Dilute Solution

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The molecular weight determination of polymethyl acrylate fractions was made in butanone by light scattering and in toluene by osmometry. Intrinsic viscosity measurements on these fractions were made in various solvents. It was found that polymethyl acrylate was degraded spontaneously in a long period (one year). Theta solvents for this polymer were searched out; isoamyl acetate and 2-methyl cyclohexanol were found to attain the Theta point at 61.7° and 56.5°C, respectively. The molecular weight and viscosity data obtained in butanone can be reproduced well by

$$[\eta]_{30^\circ\text{C}} = 3.97 \cdot 10^{-5} M_w^{0.77}$$

$$\text{and } [\eta]_{30^\circ\text{C}} = 5.37 \cdot 10^{-5} M_n^{0.76}$$

in the unit of dl.g^{-1} .

On the other hand, using the Theta point viscosities, $[\eta]_\theta$, determined in the two Theta solvents and also in a Theta solvent mixture of butanone and isopropanol (1:1 by volume), we calculated the values of $[\eta]_\theta/M_w^{1/2} (=K)$ which were proportional to the unperturbed dimension. An average value, $10^2 K = 7.0$, obtained from the viscometric data was in fair agreement with that estimated from the light scattering data. On this basis, it is concluded that the unperturbed dimension of polymethyl acrylate is far larger than that of polymethyl methacrylate. In addition, the long-range interaction parameter is discussed in view of the size of pendent group attached to polymer chains of (alkyl methacrylate)-type and (α -substituted methyl acrylate)-type.

INTRODUCTION

Although a number of conformational and thermodynamic studies on polystyrene and polymethyl methacrylate in dilute solution have been made, only a little attention has been paid to polymethyl acrylate (PMA). Polymethyl acrylate differs from polymethyl methacrylate (PMMA) at the point that no α -methyl group exists. This situation is quite similar to that for polyethylene and polypropylene, and it may be expected that the unperturbed chain dimension and other thermodynamic behavior in solution will be affected by α -methyl group¹⁾. In fact Kotera *et al.*^{2,3)} have pointed out that the chain dimension of PMA was considerably larger than that for PMMA despite the effect of α -methyl group which might influence the internal rotation. In contrast to this finding, data of molecular weights and intrinsic viscosities in a Theta solvent reported by Takahashi *et al.*⁴⁾ suggest no significant difference in the unperturbed dimensions of these polymers. This was, however, obtained by determining the statistical radius and the mo-

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molecular weight by light scattering, and a further inquisition might be necessary.

This communication deals with solution properties of PMA in a hope to inquire again the data seen in literatures and to give reliable data of PMA for discussing another series of our experimental results on styrene-methyl acrylate copolymers⁵⁾.

EXPERIMENTAL AND RESULTS

Materials. MA monomer was purified three times by distillation under nitrogen atmospheric pressure after having been dried with sodium sulfate anhydride. Two polymerization runs were made at 50°C with acetone and α, α' -azo-bis-isobutyronitrile as solvent and initiator, respectively. The polymerization condition is summarized in Table 1. Each polymerization product was fractionated into seven

Table 1. Polymerization data.

Sample code	Initiator (wt. %)	Solvent	Monomer conc. wt. %	Temp. (°C)	Time (min.)	Conversion (%)
PMA-1	0.40	Acetone	60.0	50	195	20
PMA-2	0.20		40.0	50	555	3.6

fractions at 30°C using a system butanone and methanol-water mixture as solvent and precipitant, respectively. The recovering of polymer from solution phase was extremely complicated, because the precipitate was too rubbery and sticky to be dried completely. A convenient procedure was, however, found; this is to recover the polymer in a porous precipitate that appears when the solution phase is poured into boiling water.

Solvents used for viscosity, osmotic pressure and light scattering measurements were butanone, benzene, toluene, diethyl malonate, isoamyl acetate (iAA) and 2-methyl cyclohexanol (2MCH). All the solvents were purified by the method relevant to each, except for 2MCH which has two steric isomers of *cis* and *trans* forms. Separation of these isomers was impossible, and the ratio of the optical densities at 970 and 1030 cm^{-1} , which are characteristic of the *trans* and the *cis* form, respectively⁶⁾, was used as a measure for the composition of stereoisomers. Attention was paid so as to use the solvent having the almost same infrared ratio, which ranged from 1.13 to 1.14. Such a precaution is especially important, since 2MCH is used here as a Theta solvent⁷⁾.

Light Scattering Measurements. A modified photometer of the Brice type (a Shimadzu light scattering photometer) was used for the measurement. Details of the calibration procedure and other experimental techniques have been described in previous papers^{5,8)}. Specific refractive index increment, (dn/dc), was determined in butanone at 30°C with a differential refractometer of the Brice type (Shimadzu Seisakusho Co., Ltd., Kyoto). The result was 0.097 for 436 $\text{m}\mu$ which was in good agreement with that reported by Nomura and Iwachido⁹⁾. Value of dn/dc in isoamyl acetate was estimated by extrapolating the relationship between dn/dc and

styrene (ST) content established for ST-MA random copolymers to zero ST-content; this was 0.077 at 30°C. We used this value for light scattering measurements of PMA in isoamyl acetate (Theta solvent), neglecting its temperature dependence. The final light scattering data were treated according to the Zimm plot. An example of this plot is shown in Fig. 1. The weight average molecular weights thus obtained in butanone are given in Table 2 together with the second virial coefficient, A_2 , and the statistical radius, $\langle S^2 \rangle_z$.

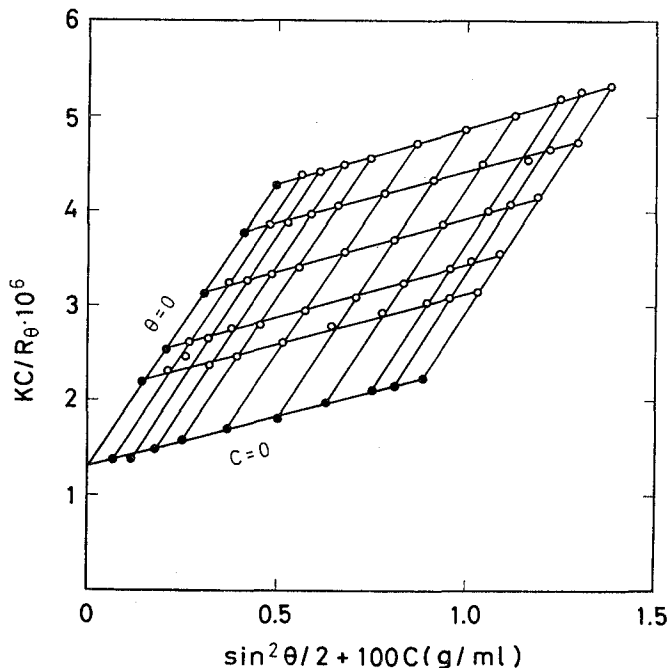


Fig. 1. Zimm's plot for PMA fraction (PMA-1-4) in butanone at 30°C.

Table 2. Characterization of sample polymers by light scattering and osmometry.

Sample	L.S. ^{a)} in butanone			O.S. ^{b)} in toluene		M_w/M_n
	$M_w \cdot 10^{-4}$	$A_2 \cdot 10^4$	$S^2 \cdot 10^{12}$ (cm ²)	$M_n \cdot 10^{-4}$	$A_2 \cdot 10^4$	
PMA-1*)	80.0	3.20				
PMA-1-1	188	1.99	54.2	136	1.23	1.4
-2	135	2.54		108	1.28	1.3
-3	109	2.53	27.4	81.3	1.27	1.3
-4	76.5	3.04	16.9	62.6	1.29	1.2
-5	51.3			39.2		1.3
-6	25.3	3.04	7.64	15.1	2.00	1.7
PMA-2*)	74.6	3.64				
PMA-2-2	170	2.65	49.8			
-3				98.0	1.49	
-6	41.7	3.03	9.10	26.3	1.31	1.6
-7	28.8	3.38				

a) Light scattering

b) Osmometry

*) Whole polymers

Osmotic Pressure Measurements. The measurement was conducted in toluene at 30°C by a Mechrolab high speed membrane osmometer. Ultracellafilters of grade "feinst" and "aller-feinst" were used as semi-permeable membrane. The osmotic plot, π/c vs. c , was almost linear for all the fractions. The plots for the fractions of PMA-1 are shown in Fig. 2. The result is summarized also in Table 2.

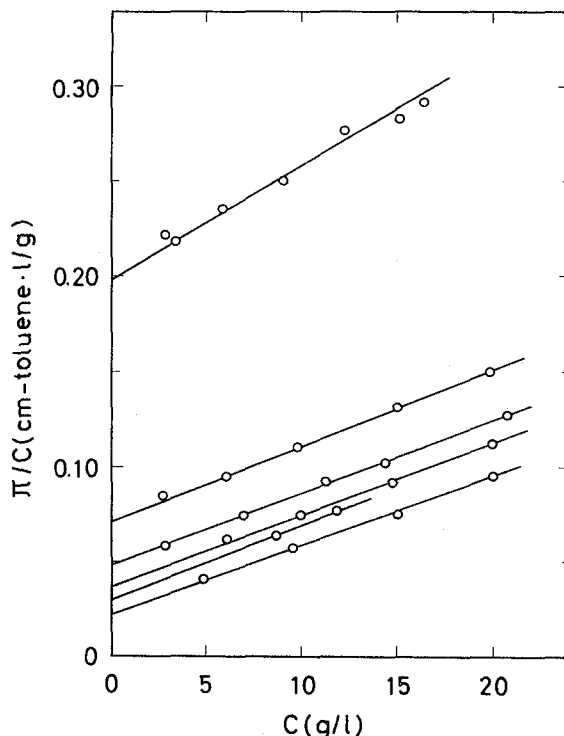


Fig. 2. Osmotic plots of π/c vs. c in toluene at 30°C for six fractions of PMA (from bottom to top, PMA-1-1, -1-2, -1-3, -1-4, -1-5 and -1-6).

Theta Temperature Determination. A semi-empirical turbidimetric method proposed by Cornet and Ballegooijen¹⁰⁾ was applied. The detail of the procedure is given in a previous paper⁹⁾. 2-Methyl cyclohexanol, isoamyl acetate, 2-ethoxyethanol and 2-butoxyethanol have been found to be suitable Theta solvents for PMA.

According to Cornet and Ballegooijen, the absolute temperature, T_c , at which the incipient turbidity is observed, is determined as a function of the volume fraction of polymer, v_2 . Figure 3 illustrates plots between $(T_c)^{-1}$ and $\log v_2$ for PMA in isoamyl acetate (iAA) and also in 2-methyl cyclohexanol (2MCH). When this plot is extrapolated to $v_2=1$, the limiting value should give the reciprocal of Theta temperature. Theta temperatures found for iAA and 2MCH were 61.7° and 56.5°C, respectively. These Theta points were further ensured by light scattering measurements made at different temperatures. Figure 4 shows the plot between A_2 and $T(^{\circ}\text{C})$ observed with PMA-1 in iAA, and one sees that the Theta temperature determined by the turbidimetric method is in good agreement with that by light scattering.

Viscosity Measurements. Ubbelohde-dilution viscometers, efflux times of which are

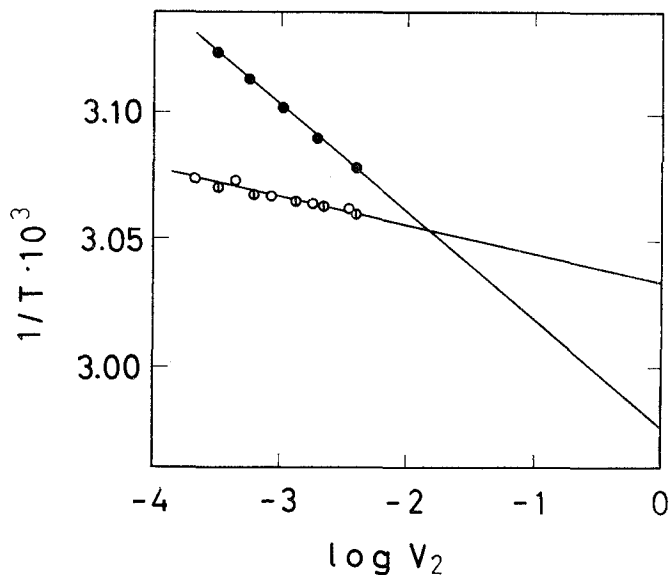


Fig. 3. Plots of reciprocal of clouding temperature ($^{\circ}\text{K}$) *vs.* logarithm of volume fraction of polymer. Circles (\bigcirc and $\textcircled{\textcircled{O}}$) refer to the determination in 2-methyl cyclohexanol, and filled circles refer to that in isoamyl acetate.

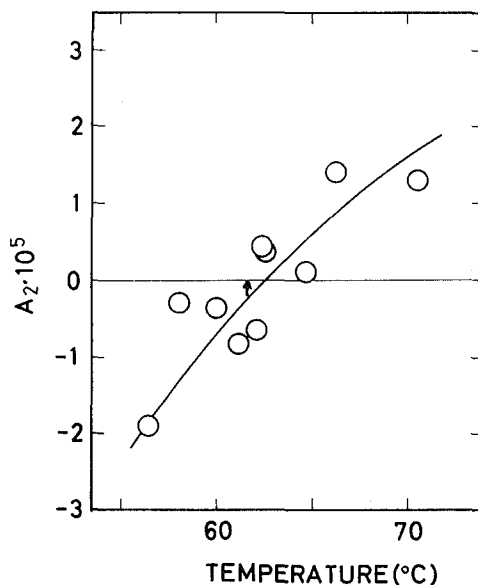


Fig. 4. Light scattering second virial coefficients as a function of temperature ($^{\circ}\text{C}$). Arrow indicates the Theta temperature found by the turbidimetry.

larger than 100 sec. (per 2 ml) for each solvent tested, were used. No kinetic energy correction was taken into account. The temperature was kept to within $\pm 0.02^{\circ}$ at 30°C . The viscosity data were plotted according to the Schulz-Blaschke equation:

$$\eta_{sp}/c = [\eta] + k'[\eta]\eta_{sp}, \quad (1)$$

where η_{sp}/c , $[\eta]$ and k' are the reduced specific viscosity, the intrinsic viscosity

Polymethyl Acrylate in Dilute Solution

and the Huggins constant, respectively. Values of $[\eta]$ and k' are given in Table 3 including data obtained in a solvent mixture of butanone and isopropanol (1:1 by volume), which has been found by Takahashi *et al.* as a Theta solvent¹⁾.

Table 3. Vales of $[\eta]$ and k' for PMA in various solevnts at 30°C.

Sample Code	$[\eta]$ (dl/g)					k'				
	(1)	(2)	(3)	(4)	(5)	(1)	(2)	(3)	(4)	(5)
PMA-1*)	1.83 ₀	1.45 ₉				0.269	0.330			
PMA-1-1	3.63 ₉	2.63 ₉	1.78 ₅	3.25 ₉	0.97 ₅	0.277	0.297	0.336	0.229	0.600
-2	2.82 ₃	2.20 ₃	1.46 ₀			0.146	0.311	0.288		
-3	2.35 ₀	1.82 ₂	1.28 ₄	2.07 ₆	0.77 ₆	0.299	0.300	0.347	0.287	0.561
-4	1.82 ₂	1.42 ₅	1.00 ₅	1.65 ₈	0.64 ₅	0.307	0.260	0.383	0.272	0.535
-5	1.25 ₂	1.03 ₅	0.73 ₅	1.20 ₀	0.51 ₀	0.328	0.300	0.414	0.300	0.520
-6	0.73 ₀	0.59 ₁	0.44 ₈			0.366	0.342	0.489		
PMA-2*)	1.69 ₅					0.261				
PMA-2-2		2.77 ₇					0.272			
-3		1.97 ₀					0.304			
-6		0.84 ₆					0.331			
-7		0.63 ₉					0.340			

(1) Benzene (4) Diethyl malonate
 (2) Butanone (5) Mixture of butanone and isopropyl alcohol (Theta solvent)
 (3) Toluene *) Whole polymers

After about one year since the above measurements has been done, we determined again the intrinsic viscosities in Theta solvents newly found, *i.e.* iAA and 2MCH. The result suggested, however, that the values of $[\eta]$ were decreased to considerable degrees, as summarized in Table 4. Thus the molecular weight determination has been again conducted by light scattering, and the $[\eta]$ - M_w relationship has been constructed. The result is consistent with that obtained previously, implying that no changes other than the chain degradation happened.

Table 4. Result of redetermination of M_w and $[\eta]$ for PMA fractions—
Effect of spontaneous degradation of PMA.

	$M_w \cdot 10^{-4}$	Degree of degradation (%)	$[\eta]$ in			
			(1) 30°C	(2) 30°C	(3) 56.0°C	(4) 62.5°C
PMA-1-1	156	17.0	—	—	—	0.842
-2	104	23.0	1.819	—	0.732	0.689
-3	90.0	17.4	—	0.702	0.655	0.639
-4	67.1	12.3	—	0.577	0.530	0.522
-5	41.9	18.3	0.972	—	0.440	0.445
-6	21.5	15.0	—	—	—	0.310
PMA-2-2	115 ^{a)}	—	2.263	—	—	—
-7	13.5 ^{a)}	—	0.498	—	—	—

- (1) Butanone
 (2) Mixture of butanone and isopropyl alcohol.
 (3) 2-methyl cyclohexanol
 (4) Isoamyl alcohol
^{a)} obtained by osmometry (M_n).

DISCUSSION

$[\eta]$ - M Relationship. Plots between $\log [\eta]$ and $\log M$ in butanone are shown in Fig. 5. This relationship established on the M_w -base is in good agreement with that given by Kotera *et al.*³⁾ within a limited molecular weight span (2.6×10^5),

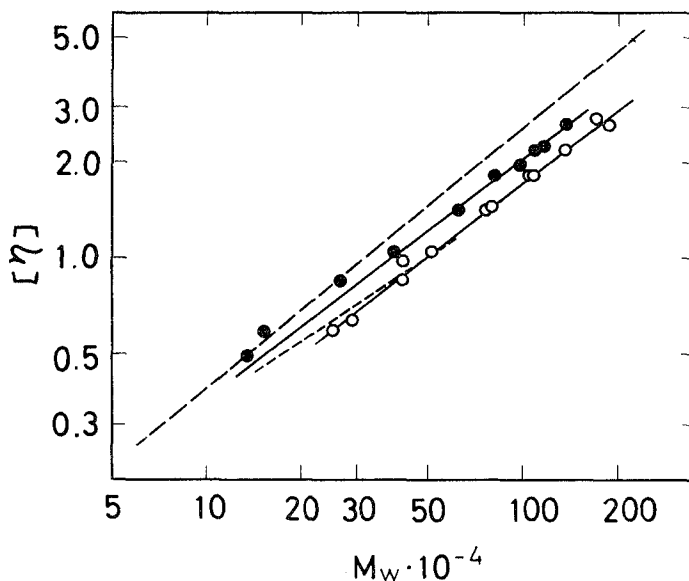


Fig. 5. Plots between $[\eta]$ and M_w (○) [M_n (●)] for PMA fractions in butanone at 30°C. Dotted and broken line refer to the results reported by Kotera *et al.* at 25°C (M_w -base)³⁾ and by Soboleva *et al.* at 20°C (M_w -base)¹¹⁾, respectively.

but in disagreement with that given by Soboleva *et al.*¹¹⁾. Our result may be reproduced by

$$[\eta]_{30^\circ\text{C}}(\text{dl/g}) = 3.97 \cdot 10^{-5} M_w^{0.77}. \quad (2)$$

For the M_n -base we have

$$[\eta]_{30^\circ\text{C}} = 5.37 \cdot 10^{-5} M_n^{0.76}. \quad (3)$$

The same plots established in benzene are shown in Fig. 6. The relationship on the M_w -base is in excellent agreement with that given in literature¹²⁾ for a wide molecular weight span, while the relationship on the M_n -base is in disagreement with that given by Guzman¹³⁾. This difference may be attributed to the difference in the polydispersity of the samples used. Figure 7 concerns the same plots in toluene and in dimethyl malonate. According to these experimental results, values of K' and a in $[\eta] = K'M^a$ are evaluated and listed in Table 5.

Figure 8 shows the same plots of the data obtained in three Theta solvents, 2MCH, iAA and the solvent mixture of butanone and isopropanol. The data points obtained in 2MCH at 56.0°C and in iAA at 62.5°C fall on a common line with a slope of 0.5, while those in the mixed solvent are in disagreement with those reported by Takahashi *et al.*,⁴⁾ which are represented by a broken line in Fig. 8.

Unperturbed Dimension. On the basis of the Flory-Fox viscosity equation^{14,15)}

Polymethyl Acrylate in Dilute Solution

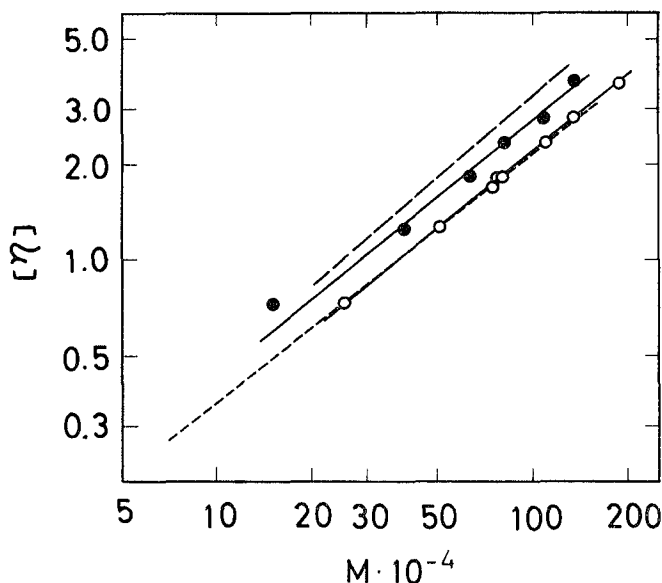


Fig. 6. Plots between $[\eta]$ and M_w (\circ) [M_n (\bullet)] for PMA fractions in benzene at 30°C. Dotted and broken line refer to the results obtained at 30°C (M_w -base)¹²⁾ and reported by Guzman at 25°C (M_n -base)¹³⁾, respectively.

Table 5. Values of K' and a for PMA in various solvents at 30°C.

	$K' \cdot 10^5$ and a								Molecular wt. range $M \cdot 10^{-4}$
	benzene		butanone		toluene		DEM ^{*)}		
M_w -base	3.5 ₆	0.79 ₈	3.9 ₇	0.77 ₂	7.7 ₉	0.69 ₇	3.5 ₁	0.79 ₃	20-200
M_n -base	4.5 ₉	0.79 ₅	5.3 ₇	0.76 ₄	9.4 ₆	0.69 ₇	5.6 ₀	0.77 ₆	15-150

*) Diethyl malonate

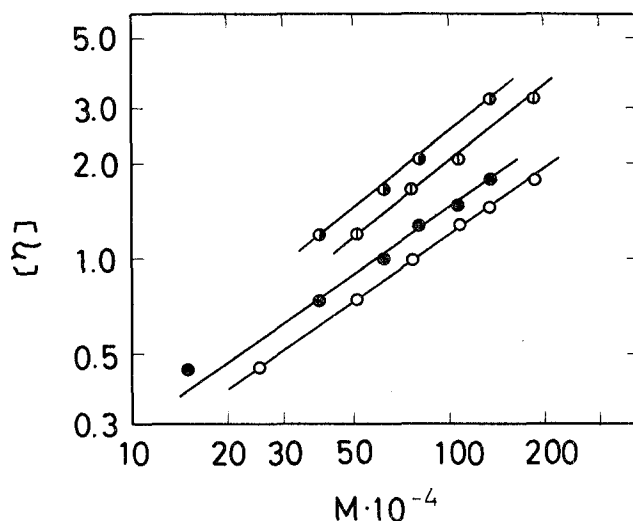


Fig. 7. Plots between $[\eta]$ and M_w (\circ) [M_n (\bullet)] for PMA fractions in two solvents at 30°C. Circles (\circ , \bullet , \circ and \bullet) indicate the plots obtained in diethyl malonate (M_w - and M_n -base), in toluene (M_w - and M_n -base).

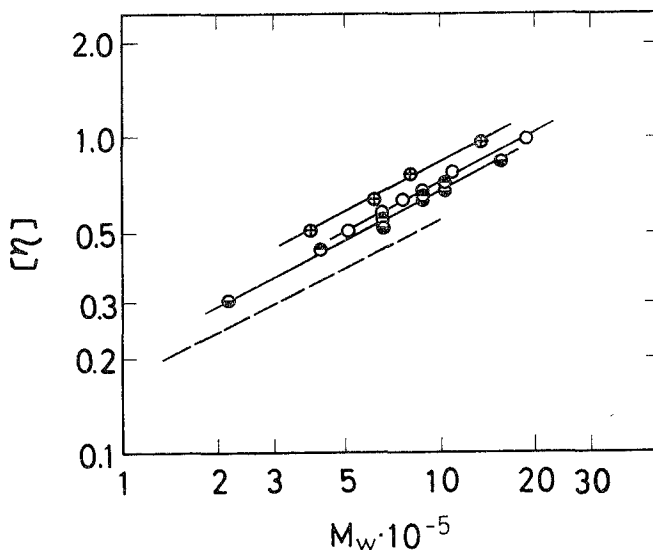


Fig. 8. Plots of Theta point viscosity against molecular weight for PMA. Circles (\oplus , \circ , \odot and \otimes) indicate the plots obtained in mixed Theta solvent of isopropyl alcohol and butanone (M_n -base) at 30°C , the same solvent (M_w -base), 2-methyl cyclohexanol at 56.0°C , and isoamyl acetate at 62.5°C , respectively. Broken line refers to the result reported by Takahashi *et al.*⁴³. For the details, see text.

$$[\eta] = KM^{1/2}\alpha_\eta^3 \quad (4)$$

$$\text{with } K = \phi_0(6\langle S^2 \rangle_0/M)^{3/2} = \phi_0 A^3, \quad (5)$$

the unperturbed dimension (or the short-range interaction parameter), A^2 , may, be easily estimated with the Theta point viscosity, $[\eta]_\theta$. Here ϕ_0 and $\langle S^2 \rangle_0$ are the Flory viscosity constant at Theta point, the most recent value for which is $2.68 \cdot 10^{23}$ (c.g.s.),¹⁶⁾ and the unperturbed mean square statistical radius, respectively.

In general the K value differs in accordance with the nature of molecular weight average, *i.e.* for M_n and M_w . Hereafter we discuss the K value on the basis of M_w . From the values of M_w and $[\eta]_\theta$ found in 2MCH and iAA, $K_w = [\eta]_\theta / M_w^{1/2}$ can be readily calculated. This leads to $10^2 K_w = 6.8$, which is somewhat different from 5.4 reported by Takahashi *et al.* in the mixed Theta solvent³⁾. Our re-examination using this solvent resulted in 7.2, and the value of 7.0 seems reasonable as the average.

In this connection we have estimated the K value with data of the statistical radius $\langle S^2 \rangle_z$, obtained for unfractionated sample PMA-1 in iAA in the proximity of Theta point (61.7°C). The statistical radii evaluated at different temperatures were plotted against temperature in Fig. 9 and the value at the Theta point was determined by interpolation of the above result. Here we neglected two data points which exist far apart from the averaged line (see Fig. 9). In consequence, the value of $\langle S^2 \rangle_{\theta z}$ given in the previous paper⁵⁾ differs from the present value a little bit. The result was $10^{12} \cdot \langle S^2 \rangle_{\theta z} = 8.1 \text{ cm}^2$. This value was converted to the K_w value with the aid of Eq. (5), assuming $\phi_0 = 2.5 \cdot 10^{23}$ (c.g.s.) and $M_w/M_n = 2$. This leads to $10^2 \cdot K_w = 7.0$, which is in fair agreement with that estimated from the viscosity data. This comparison confirms well a previous conclusion drawn by Kotera *et al.*^{2,3)} that the K value for PMMA ($5.3 \cdot 10^{-2}$)¹⁷⁾ is far smaller than

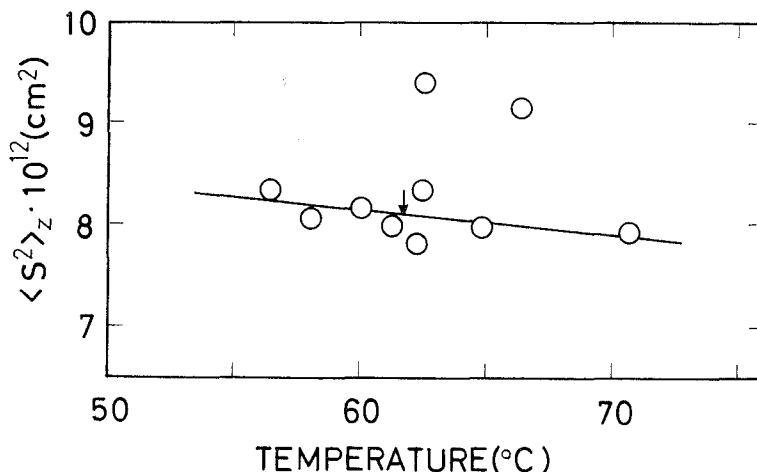


Fig. 9. Mean-square statistical radii of PMA-1 in the proximity of Theta point as a function of temperature, solvent: isoamyl acetate. For the details, see text.

that for PMA, though this seems somewhat contradictory if one takes the effect of methyl group upon the internal rotation into consideration. However the steric factor, σ , defined by

$$\sigma^2 = A^2/A_f^2 \quad (6)$$

is indifferent from each other. The σ values are 1.89 and 1.92 for PMMA and PMA respectively.

Evaluation of Short-range and Long-range Interaction Parameters. According to the Stockmayer-Fixman theory, the intrinsic viscosity is represented by the following equation

$$[\eta] = KM^{1/2} + 0.51\phi_0 BM \quad (7)$$

where A and B are the short-range and long-range interaction parameter, respectively^{15,18}. Plots of $[\eta]/M_w^{1/2}$ vs. $M_w^{1/2}$ based on Eq. (7) are shown in Fig. 10. The K value obtained in good solvents from the intercepts on ordinate is in good agreement with those obtained in Theta solvents.

On the other hand, the statistical radius of polymer is given by

$$(6\langle S^2 \rangle / M)^{3/2} = A^3 + 0.632BM^{1/2} \quad (8)$$

with the two parameters, A and B ^{15,19}. The plot according to Eq. (8) is given in Fig. 11. In constructing this figure, the z -averaged statistical radius, $\langle S^2 \rangle_z$, determined by light scattering was converted to the weight averaged value $\langle S^2 \rangle_w$ by assuming the exponential distribution of molecular weight, expressed in

$$\langle S^2 \rangle_w = [(h+1)/(h+2)] \langle S^2 \rangle_z \quad (9)$$

$$M_n/h = M_w/(h+1) = M_z/(h+2), \quad (10)$$

with $h=2.5$, corresponding to $M_w/M_n=1.4$.

To get a supplementary evidence for approving the values of A and B obtained above, data from another source will be used. According to Kurata *et al.*,²⁰ the second virial coefficient A_2 may be written approximately by

$$A_2 = 1.65 \cdot 10^{23} (A^3/M^{1/2}) + 0.968 \cdot 10^{23} B \quad (11)$$

A plot of $A_2M_w^{1/2}$ vs. $M_w^{1/2}$ found in butanone is shown in Fig. 12. Thus we may

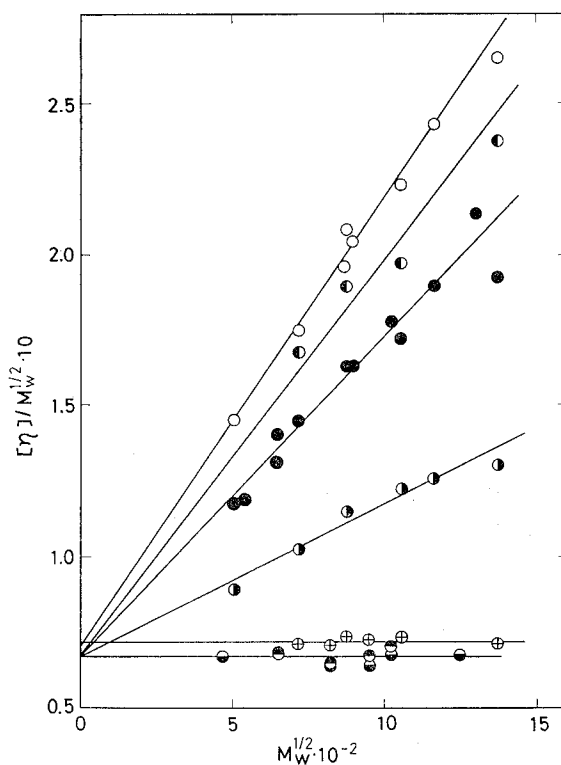


Fig. 10. Stockmayer-Fixman plots for PMA in benzene (○), in diethyl malonate (◐), in butanone (●), in toluene (◑), in mixed solvent of butanone and isopropyl alcohol (⊕) at 30°C; 2-methyl cyclohexanol (⊙) at 56.0°C and in isoamyl acetate (⊗) at 62.5°C.

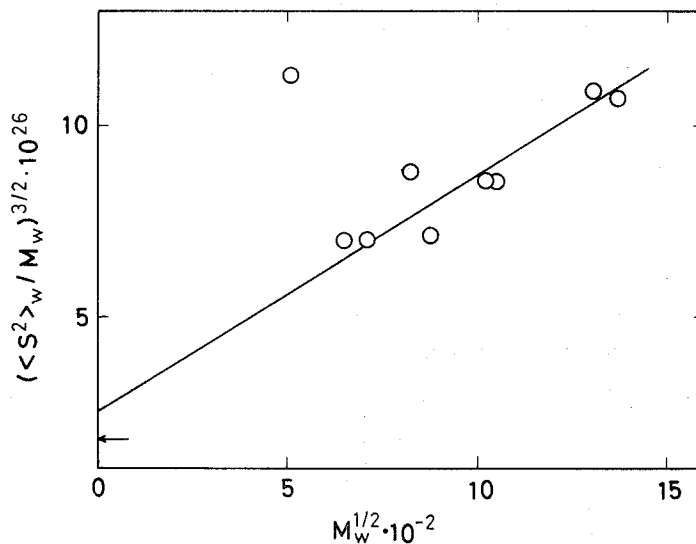


Fig. 11. Plots according to Eq. (8) for PMA in butanone at 30°C. Arrow indicates the value corresponding to $A = 6.36 \times 10^{-9}$ obtained from viscosity data. For the details, see text.

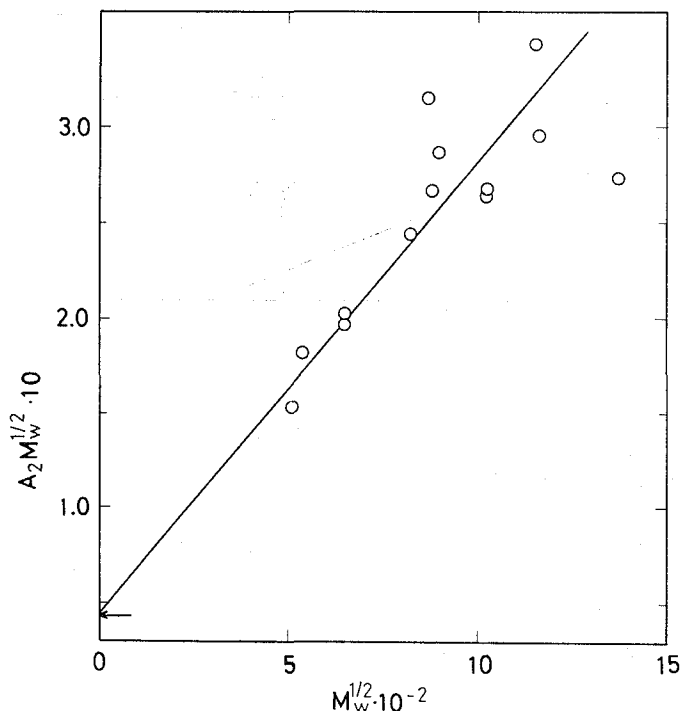


Fig. 12. Plots according to Eq. (11) for PMA in butanone at 30°C. Arrow indicates the same value as shown in Fig. 11. For the details, see text.

compare the values of A and B from different sources. As Table 6 indicates, the A values derived from these sources are in good agreement with each other, while the B value obtained from the viscosity data is far lower than those from the other two methods, as such has been reported by various authors.

Table 6. Short-range and long-range interaction parameters, A and B , obtained by different methods.

Method	$A \cdot 10^9$	$B \cdot 10^{28}$
from $[\eta]$, Eq.(7)	6.3 ₆	7.7 ₀
from $\langle S^2 \rangle$, Eq.(8)	7.1 ₅	14.4
from A_2 , Eq.(11)	6.4 ₃	24.5

Effect of Size of Pendent Group upon Long-range Interaction. In the last section we will discuss the effect of pendent groups attached to vinyl chain upon the long-range interaction. On the basis of $[\eta]$ and M data obtained for (alkyl methacrylate)-type²¹⁾ and (α -substituted methyl acrylate)-type²²⁾ polymers, the long-range interaction parameters, B , in butanone at 30°C, were evaluated as a function of the carbon number involved in each pendent group (see Fig. 13). The relationship between B and carbon number found for (alkyl methacrylate)-type polymers differs somewhat from that for (α -substituted methyl acrylate)-type polymers at the carbon number of unity. However, when the carbon number exceeds unity,

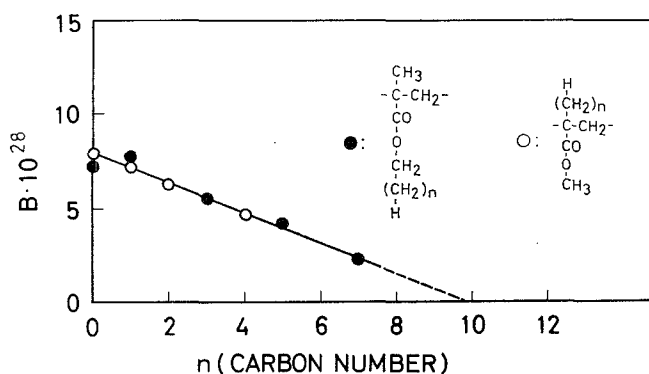


Fig. 13. Long-range interaction parameter B in butanone at 30°C as a function of carbon number, n , involved in pendent groups for (alkyl methacrylate)-type polymers (●) and (α -substituted methyl acrylate)-type polymers (○).

these relationships are superposed on a master line, and the extrapolation of this line appears to meet the abscissa at the carbon number of 10. This might suggest that butanone could be a Theta solvent for (undecyl methacrylate)-polymer and its Theta point would exist at 30°C .

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Polymethyl Acrylate in Dilute Solution

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